

The Equation of State in Layered Structure of High Temperature Superconductors with 2223 System

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ABSTRACT

In this paper the problem of equation of state of new high temperature superconductors is discussed. This problem can only be solved with the help of thermodynamic variables. Now such a set of variable is only available in the phases in the 2223 system. In this system phase equilibria have been establish and the stability of the superconducting materials and equation of states established.

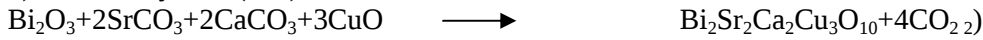
Keywords: Entropy, superconductivity, enthalpy.

INTRODUCTION

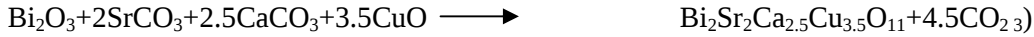
Since the discovery of the Bi-Sr-Ca-Cu-O superconducting compounds [Maed *et al.*, 1988]¹, a great deal of work has been done to prepare the high critical temperature (T_c) phases. The most common method used to synthesize these superconducting oxides is the solid state reaction method [Koyoma *et al.*, 1988]², which consist of the mixing nominal composition of high purity compounds such as Bi_2O_3 , SrCO_3 , CaCO_3 and CuO . The Bi-2223 phase has attracted considerable interest due to its higher T_c and the potential for applications. One of the reasons for the low critical current densities J is the granular nature of this sintered high

temperature superconducting (HTS) compound. It is difficult to prepare single phase material for Bi-2223 phase. [Kovaleva *et al.* 2004]³ presented systematic study of the c-axis lattice dynamics in $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ ($n=1, 2, 3$) cuprate superconductors (Bi2201, Bi2212 and Bi 2223) based on spectral ellipsometry investigation on single crystal and comparing them with theoretical shell model calculation. The samples were prepared by the solid state reaction method using highly pure 99.99% powders of Bi_2O_3 , SrCO_3 and CaCO_3 , CuO , with appropriate weights in proportion to their molecular weights through the following chemical reactions [Wida M. Faisal *et al.*]⁴.

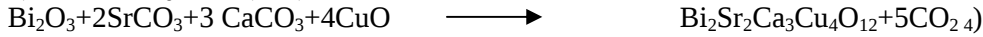
1) The first system (n, 3)



2) The second system (n, 3.5)



3) The third system (n, 4)



4) The fourth system (n, 4.5)

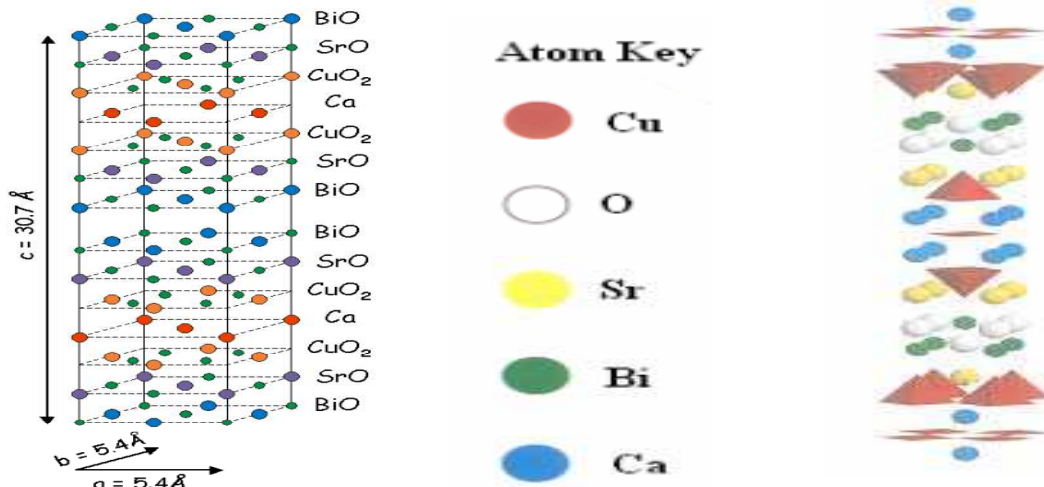
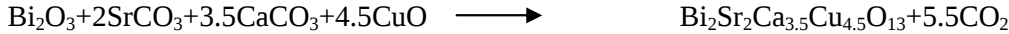


Fig.1 Crystal structure of Bi – 2223

Four type of superconductors systems were obtained, namely, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\delta}$, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\text{Pb}}$, $\text{Bi}_2\text{Sr}_2\text{Ca}_{2.5}\text{Cu}_{3.5}\text{O}_{11+\text{Pb}}$, $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_{12+\text{Pb}}$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_{3.5}\text{Cu}_{4.5}\text{O}_{13+\text{Pb}}$. These superconductors are in layer forms as shown in fig-1 from [R. J. Cava *et al.* 1988]⁵. The thickness of the layers is not fixed. But these layer are variables due to Temperature (T), Volume (V) and Pressure (P) [Moore, J. W]⁶. Since the entropy is a state function. Its value will depend on any two of the three variable. The combination of variables will be either T and T or P.

Therefore entropy is a function of temperature and volume. So

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (1)$$

Combined form of first and second law of thermodynamics is

$$dE = TdS - PdV \quad (2)$$

But internal energy (E) is also a function of T and V

$$E = E(T, V)$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad (3)$$

Substituting the value of dE in equation (2) and we get,

$$TdS = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV$$

$$TdS = \left(\frac{\partial E}{\partial T}\right)_V dT + \left\{ \left(\frac{\partial E}{\partial V}\right)_T + P \right\} dV \quad (4)$$

Comparing the coefficients of equations (1) and (4) then

$$T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \quad (5)$$

and

$$T \left(\frac{\partial S}{\partial T}\right)_T = - \left(\frac{\partial E}{\partial V}\right)_T + P \left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial T}\right)_V - P \quad (6)$$

Differentiating equation (6) with respect to T at constant volume,

$$\left(\frac{\partial^2 E}{\partial T \partial V}\right) = T \left(\frac{\partial^2 S}{\partial T \partial V}\right) + \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V \quad (7)$$

Equation (2) can be written as at constant volume

$$\left(\frac{\partial E}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad (8)$$

Differentiating equation (8) with respect to V at constant temperature T .

$$\left(\frac{\partial^2 E}{\partial T \partial V}\right) = T \left(\frac{\partial^2 S}{\partial T \partial V}\right) \quad (9)$$

From equation (7) and (9) we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (9a)$$

Substituting the value of $\left(\frac{\partial S}{\partial T}\right)_V$ from equation (8) and $\left(\frac{\partial S}{\partial V}\right)_T$ from equation (9a) into equation (1) we get.

$$dS = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV \quad (10)$$

This equation is applicable to layered high temperature superconductors of 2223 system.

Again entropy is a function of temperature (T) and (P)

$$S = S(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (11)$$

Since enthalpy of the system

$$H = E + PV \quad (12)$$

From equation (2)

$$T dS = d(H - PV) + P dV$$

$$= dH - V dp \quad (13)$$

Since H is also a function of T and P

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (14)$$

Substituting the value of d from equation (14) in to (13).

$$T dS = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP - V dP \quad (15)$$

Comparing the coefficients of equations (15) and (13)

$$T \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \quad (16)$$

And

$$T \left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - V \left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \quad (17)$$

Differentiating of equation (17) with respect to T at constant P .

$$\left(\frac{\partial^2 H}{\partial P \partial T}\right) = T \left(\frac{\partial^2 S}{\partial T \partial P}\right) + \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \quad (18)$$

Differentiating of equation (17) at constant V

$$\left(\frac{\partial^2 H}{\partial P \partial T}\right) = T \left(\frac{\partial^2 S}{\partial T \partial P}\right) \quad (19)$$

From equation (18) and (19)

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P \quad (20)$$

Substituting $\left(\frac{\partial S}{\partial P}\right)_P$ from equation (16) and $\left(\frac{\partial S}{\partial P}\right)_T$ from equation (20) in equation (11) we get

$$dS = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P dT - \left(\frac{\partial V}{\partial T} \right)_P dP \quad (21)$$

Again this equation is applicable to layered high temperature superconductor in 2223 system.

DISCUSSION AND CONCLUSION

This is the macroscopic theory of layered high temperature superconductor. We use equation (21) to calculate the difference of the entropy normal and superconducting states and we get consequences if temperature tends to zero, Difference in entropy is also zero therefore the superconducting state is not ordered than the normal state and phase transition will take place of the high temperature superconductor. Therefore at critical temperature, transition takes place without absorption or emission of heat. We can also estimate the difference in specific heat of HTS. Since in the theory of superconductivity, the idea exists that any superconductor is a thermodynamically unstable system (W. L. Johnson)⁷. A multilayer superconductors (whose entropy will change), is reported by [Ideta *et al.*]⁸ and [H.S. Singh, Rohitash Kumar]⁹. Entropy is the property of high temperature superconductor (HTS). Equation of state reveals that the layers is form in equilibrium.

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